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Patents ADP number (if you know it)

① 78894/3002

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

② 6254866003

4. Title of the invention

METHOD FOR SOIL REMEDIATION AND ENGINEERING

5. Name of your agent (if you have one)

Stevens Hewlett & Perkins

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Description 9

Claim(s)

Abstract

Drawing(s) 1 + 1

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STEVENS HEWLETT & PERKINS

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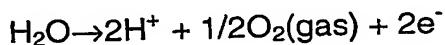
METHOD FOR SOIL REMEDIATION AND ENGINEERING

This invention relates to a method for electrokinetic soil remediation and engineering, and, more particularly, to such a method
5 which involves the strategic electokinetic placing of an iron-rich barrier in soils, sediments and slurries.

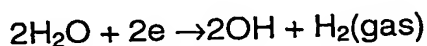
Contaminated soils and groundwater at industrial, waste disposal and spill sites are serious environmental problems. Although
10 clays and silts tend to sequester large quantities of heavy metals, radionuclides, and selected organic pollutants (e.g., Kovalick 1995), they are resistant to remediation with traditional technologies because of their low hydraulic conductivities. Electrokinetics is a process that separates and extracts heavy metals, radionuclides, and organic, inorganic, BTEX and radioactive wastes (e.g., Acar & Alshawabkeh 1993; Kovalick 1995;
15 Virkutyte *et al.*, 2002).

The electrokinetic process involves a low intensity direct current (DC) applied across electrode pairs that have been implanted on
the ground each side of the contaminated soil mass. When DC electric fields are applied to contaminated soil via electrodes placed into the
20 ground, migration of charged ions occurs. Positive ions move towards the negatively charged cathode, while negative ions are attracted to the positively charged anode. It has been shown that non-ionic species are transported along with the electro-osmotically-induced water flow. Electrokinetic remediation is possible in both saturated and unsaturated
25 soils.

The dominant and most important electron transfer reaction that occurs at the electrodes during the electrokinetic process is the electrolysis of water:-



30



The electric current causes electro-osmosis and ion migration, which moves the aqueous phase contaminants in the subsurface from one electrode to the other. Contaminants in the aqueous phase, or
5 desorbed from soil particles are transported towards respective electrodes depending on their charge. Commonly, contaminants are extracted by a secondary recovery system or deposited at the electrode. Recovery methods for contaminants that have migrated to the electrodes include electroplating, precipitation/co-precipitation, pumping near the electrode, or
10 complexing with ion exchange resins. Surfactants, complexing agents and reagents are frequently used to assist contaminant movement (e.g., Kovalick 1995; Virkutyte et al., 2002). However, most contaminated sites contain mixtures of wastes rather than single contaminants, which makes the decontamination process more complicated, and at present there is no
15 standardised universal soil/sediment remediation approach.

Electrodes that are inert to anodic dissolution are conventionally used in electrokinetic soil remediation. There include graphite, platinum, gold and silver electrodes, although less expensive electrodes made from titanium, stainless steel and plastic have also been
20 employed. Metals such as lead, chromium, cadmium, copper, uranium, mercury and zinc, as well as polychlorinated biphenyls, phenols, chlorophenols, toluene, trichloroethane and acetic acid are suitable for electokinetic remediation and recovery.

The main parameters that influence the overall process are
25 soil properties, depth and type of contamination, cost of accommodating electrodes and placing treatment zones, clean up time, and cost of labour (Virkutyte et al., 2002). Factors that influence the cost of the electrokinetic remediation process are soil characteristics and moisture, contaminant concentrations, concentration of non target ions and conductivity of pore
30 water, depth of the remediated soil, site preparation requirements, and electricity costs (van Cauwenberghe 1997). The cost optimised distance

between electrodes for commercial systems is 3 to 6m for most soils (Lagerman 1993; Ho et al., 1999). Given that the migration rate of contaminants is approximately 2 to 3cm/day, the time frame for successful remediation between electrodes spaced at 2 to 3m is of the order of 100 days, although cation-selective membranes are commonly employed to reduce remediation periods to 10 to 20 days (van Cauwenberghe 1997). The breakdown of costs associated with a electrokinetic remediation programme are approximately 40% for electrode construction, 10 to 15% for electricity, 17% for labour, 17% for materials, and up to 16% for licenses and other fixed costs (Ho et al., 1997).

It is an object of the present invention to provide an improved method for electrokinetic soil remediation and engineering which is low cost, efficient and flexible in its application. This is achieved by the strategic electrokinetic placing of an iron rich barrier to a) remobilise and trap contaminants in polluted soils, sediments and slurries; b) provide a physical barrier to waste spillages; and c) stabilise and strategically dewater/rewater soils.

According to the present invention there is provided a method for electrokinetic soil remediation and engineering which comprises applying a direct current across an area of soil, sediment or slurry so as to generate a pH gradient and which promotes the *in situ* precipitation of a stable iron-rich band.

The method of this invention is characterised by increasing the mobility and solubility of contaminants through the application of an electric charge and simultaneously arresting their migration by fixation to an electrochemically-generated ferric iron band which is precipitated within the area under treatment. This approach is distinct from other remediation techniques because it is geared towards deliberately producing an iron band *in situ* between the cathode and the anode, which simultaneously provides a physical as well as a chemical barrier; employs a low voltage of typically less than 0.2 volts per cm distance between electrodes (with low

energy requirements) to generate a strong pH gradient of typically from pH 2 to pH 13 within soils and sediments; uses low cost, sacrificial cathode and anode materials; can produce, through differential dewatering, controlled differential subsidence and permeability reduction; and which
5 can be generated in natural and industrial materials over laboratory timescales. In contrast, current commercial techniques have an order of magnitude higher energy requirements, actively avoid generation of a pH gradient and precipitation of iron or contaminants within the soil or sediment (e.g. current electrokinetic techniques); or use *ex situ* clean-
10 up/disposal; or hard engineering technologies (e.g. permeable reactive barriers).

The present invention is a low voltage electro-chemical based technique, which uses electrokinetics to generate an intense pH gradient (pH 2 – pH 13) in soils, sediments and sludges, destabilise/dissolve
15 minerals and force the *in situ* precipitation of a stable iron-rich band. Such iron-rich bands are found in natural rock and soil systems, where naturally occurring internal electric fields (with potential differences of the order of 1.0 to 1.5 volts) can produce bands of iron stone in unlithified sediments (e.g. Jacob *et al*, 1996). Such bands can result when the electrolytic
20 dissociation of water takes place, with the formation of an anode zone characterised by acidic ions (pH 2.0 – 2.5), and a cathode zone characterised by alkaline ions (pH 10.5 – 11.5). As a consequence of the potential difference a sharp boundary zone is developed within which an abrupt pH change from 2.5 to 8 occurs. Where sufficient iron is present in
25 the system, this is remobilised at the low pHs present in the anode zone, and spontaneously precipitated as insoluble metal hydroxides at the boundary zone of abrupt pH change (Jacob *et al*, 1996).

The method of the present invention thus emulates these natural iron^{III} mineralisation processes, but over laboratory rather than
30 geological time scales, by applying a direct electric potential to electrodes to grow bands of iron^{III} mineral phases in sediment or soil columns, and to

harness their adsorptive properties, to trap pollutants from the aqueous phase, or desorbed from soil particles during their migration in the applied electrokinetic field. Freshly precipitated amorphous or poorly crystalline Fe and Mn-rich solids, of the type generated by this method, are extremely effective scavengers of a range of heavy metals, radionuclides and organic pollutants in a variety of environments (Bendell-Young and Harvey 1992, Cundy and Croudace 1995; N.B. iron is also known to dechlorinate toxic chlorinated hydrocarbons). Moreover, because this method generates strongly acidic conditions at the anode, contaminants attached to soil or sediment particles (such as radionuclides and heavy metals), which are soluble under acidic conditions are solubilised and forced to migrate towards the cathode, and subsequently (co)-precipitated with the iron-band. In essence, the present invention provides the opportunity to "flush" contaminants from contaminated sediments (e.g. plutonium), and then retrap them in the semi-permeable iron-band. This offers the potential of *in situ* clean-up of contaminated soils, sediments and sludges. Clean-up of the whole soil volume between the electrodes can be achieved, and plating of contaminants onto the cathode avoided, by simply reversing the polarity of the electrodes at regular intervals.

The approach embodied in the method of this invention is distinct from existing *in situ* remediation technologies, such as permeable reactive barriers, in that rather than merely sequestering contaminants from solution, the system actually mobilises contaminants into solution prior to their subsequent trapping by the reactive band, thus cleaning contaminated soils as well as ground waters. It differs from existing electrokinetic techniques in its use of low-cost electrodes, its low energy requirements and most significantly in its deliberate generation of a sorptive iron-band in the material being treated. Hence, the electrokinetic technique described here is innovative and clearly distinguished from other electrokinetic treatment systems. The precipitated iron band, however, represents much more than merely a chemical sink for toxic contaminants liberated from the

sediment column via oxidation-reduction and pH reactions. The electrokinetic process that triggers iron oxyhydroxide precipitation band formation may also be used to stabilise, and massively reduce the permeability of soils and sediments through differential dewatering of clays, and iron-band generation. Hence, electrokinetic ferric iron precipitation represents a means of physically confining waste spills, providing a reactive barrier to liquid waste spillages that can be re-sealed and strengthened by periodic applications of electrical current (for instance in physically trapping and sorbing leachate that has percolated through the base liner of a landfill). In addition, the method offers the potential, through strategic dewatering or rewatering of soils and sediments and iron-band generation, to rewater and stabilise soils for civil engineering applications (e.g. in building works). Existing dewatering techniques involve complete dewatering of large-volume slurries (e.g. Lamont-Black 2001) whereas the present technique is applied *in situ* to strategically rewater or dewater parcels of soil, and so has a range of potential civil engineering applications (such as dealing with tree-induced subsidence in back gardens).

The method of this invention may have direct applicability in relation to the integrity of land fill liners, permeable reactive barrier technologies, and funnel and gate systems, controlled differential subsidence, remediation of contaminated land (soils and sediments) and clean up of contaminated industrial sludges and slurries. Consequently, it will be of significant interest and potential benefit to a wide range of organisations, for example environment agencies, water companies, land fill operators, civil engineering and environmental consultants and nuclear fuel companies.

The method of this invention will now be illustrated by the following example. Figure 1 referred to therein is a photograph which shows that by employing appropriate voltages an inert $\text{Fe}(\text{OH})^{\text{III}}$ bearing band can be strategically grown, from point sources, through *in situ* precipitation in a sediment column, approximately equidistant between

electrodes.

Example

Pilot scale studies have been applied at laboratory scales in
5 25x2x15cm and 30x50x40cm open topped perspex cells (i.e. effectively in
two dimensional and three dimensional space). All experiments have been
run at <2 volts. Electrodes were fabricated from 25mm diameter cast iron
rods (Grade 250), composition: C 3.48%, Si 2.87%, Mn 0.812%,
S 0.099%, P 0.364%, Fe REM. The first experiments, working in a thirty
10 hour time frame with well sorted water saturated sands, resulted in the
generation of a continuous vertical iron band, part of which is depicted in
Figure 1. Initial permeability of the sands was 0.48×10^{-5} m/s, post
treatment permeability was recorded at 0.19×10^{-5} m/s. Experiments have
been run on a variety of contaminated muds, with groundwater and
15 seawater interstitial pore waters, under unsaturated and saturated
conditions. Time scales range from 3 to 400 hours. In every case a 1 to
4 cm thick, coherent, iron stone was generated *in situ*, approximately
equidistant between cathode and anode. For the mud experiments, initial
permeability was typically $\sim 0.29 \times 10^{-7}$, whereas treated material
20 permeability was recorded at 10^{-9} , or less, i.e. practically impervious. In
addition, clear dewatering was consistently observed in the sediment
around the anode, and rewatering around the cathode.

Chemical analyses have concentrated on copper bearing
mud from Southampton Water. Initial copper content was recorded by AAS
25 (Atomic Absorption Spectroscopy) at 88 parts per million (ppm). A set of
three spaced electrode pairs arranged 22cm apart were inserted. A
coherent, extractable, ironstone band with a thickness of up to 3cm was
generated from the point sources. The band occupied 14% of the cross
sectional area of the treated area. After 390 hours (16.3 days) of
30 electrokinetic treatment, the anode zone sediment showed a greater than
55% reduction in copper content (note that a proportion of the copper

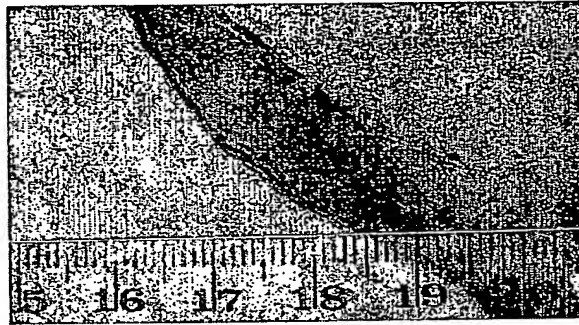
present is natural background copper, locked away in stable mineral interiors). Hydrocarbon-rich effluent was also forced to migrate out of the mud in the cathode zone under the applied electric field. The energy requirement for the experiment was 10.9 kW/m^3 , which compares
5 extremely favourably against commonly cited energy requirements for other electrokinetic remediation systems, e.g. 500 kW h/m^3 for removal of metal contaminants (e.g. Virkutyte *et al*, 2002). The time scale for copper decontamination of the sediment is comparable in duration to existing technologies which employ comparatively expensive cation-selective
10 membranes (van Cauwenberghe 1997). Moreover, given that the cast iron used as an electrode material in the method is comparatively inexpensive (compared to standard electrodes used in other techniques, e.g. gold coated electrodes and graphite), it appears that the experimental system is low cost in terms of energy, materials and electrode construction, which
15 typically make up ~70% of the costs associated with any electrokinetic remediation system (Ho *et al*, 1997).

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Figure 1: Sub-vertical, 1cm thick Fe-rich band generated in water-saturated sands after 30 hours application of a 1.5V potential difference between cast iron electrodes.



PCT Application

GB0304181



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